Sulfur condensation curve

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SECTION 22

Sulfur Recovery

Sulfur is present in natural gas principally as hydrogen sulfide (H_2S) and, in other fossil fuels, as sulfur-containing compounds which are converted to hydrogen sulfide during processing. The H_2S, together with some or all of any carbon dioxide (CO_2) present, is removed from the natural gas or refinery gas by means of one of the gas treating processes described in Section 21. The resulting H_2S-containing acid gas stream is flared, incinerated, or fed to a sulfur recovery unit. This section is concerned with recovery of sulfur by means of the modified Claus and Claus tail gas clean-up processes. Redox processes are touched upon. For a discussion and description of other sulfur recovery processes, see Maddox[1].

THE CLAUS PROCESS

The Claus process as used today is a modification of a process first used in 1883 in which H_2S was reacted over a catalyst with air (oxygen) to form elemental sulfur and water.

$$H_2S + \tfrac{1}{2}\,O_2 \rightarrow S + H_2O \qquad \textbf{Eq 22-1}$$

Control of this highly exothermic reaction was difficult and sulfur recovery efficiencies were low. In order to overcome these process deficiencies, a modification of the Claus process was developed and introduced in 1936 in which the overall reaction was separated into (1) a highly exothermic thermal or combustion reaction section in which most of the overall heat of reaction (from burning one-third of the H_2S and essentially 100% of any hydrocarbons and other combustibles in the feed) is released and removed, and (2) a moderately exothermic catalytic reaction section in which sulfur dioxide (SO_2) formed in the combustion section reacts with unburned H_2S to form elemental sulfur. The principal reactions taking place (neglecting those of the hydrocarbons and other combustibles) can then be written as follows:

Thermal or Combustion Reaction Section

$$H_2S + 1\tfrac{1}{2}\,O_2 \rightarrow SO_2 + H_2O \qquad \textbf{Eq 22-2}$$

ΔH @ 77°F = –223 100 Btu

Combustion and Catalytic Reaction Sections

$$2\,H_2S + SO_2 \rightarrow \frac{3}{x}\,S_x + 2\,H_2O \qquad \textbf{Eq 22-3}$$

ΔH @ 77°F = – 41 300 Btu

Overall Reaction

$$3\,H_2S + 1\tfrac{1}{2}\,O_2 \rightarrow \frac{3}{x}\,S_x + 3\,H_2O \qquad \textbf{Eq 22-4}$$

ΔH @ 77°F = –264 400 Btu

This is a simplified interpretation of the reaction actually taking place in a Claus unit. The reaction equilibrium is complicated by the existence of various species of gaseous sulfur (S_2, S_3, S_4, S_5, S_6, S_7, and S_8) whose equilibrium concentrations in relation to each other are not precisely known for the entire range of process conditions. Furthermore, side reactions involving hydrocarbons, H_2S, and CO_2 present in the acid gas feed can result in the formation of carbonyl sulfide (COS), carbon disulfide (CS_2), carbon monoxide (CO), and hydrogen (H_2). Gamson and Elkins[2] cover the basic theory involved in the Claus process; however, they ignore the many potential side reactions and also the existence of S_3, S_4, S_5, and S_7.

For the usual Claus plant feed gas composition (water-saturated with 30-80 mol % H_2S, 0.5-1.5 mol % hydrocarbons, the remainder CO_2), the modified Claus process arrangement results in thermal section (burner) temperatures of about 1800 to 2500°F. The principal molecular species in this temperature range is S_2 (Fig. 22-19) and conditions appear favorable for the

FIG. 22-1

Nomenclature

H = heat content or enthalpy, Btu/lb or Btu/lb-mole

K_p = equilibrium constant

For the low pressure, vapor phase Claus reaction

$$2\,H_2S + SO_2 \rightarrow 2\,H_2O + \frac{3}{x}\,S_x$$

$$K_p = \frac{(P_{H_2O})^2\,(P_{S_x})^{3/x}}{(P_{H_2S})^2\,(P_{SO_2})} = \frac{[\text{Mols } H_2O]^2\,[\text{Mols } S_x]^{3/x}}{[\text{Mols } H_2S]^2\,[\text{Mols } SO_2]}\left[\frac{\pi}{\text{Total Mols}}\right]^{\frac{3}{x}-1}$$

LT/D = long ton per day. A long ton is 2240 pounds.

P = partial pressure, atmospheres

π = total pressure, atmospheres

Acid Gas: feed stream to sulfur recovery plant consisting of H_2S, CO_2, H_2O, and usually less than 2 mol % hydrocarbons.

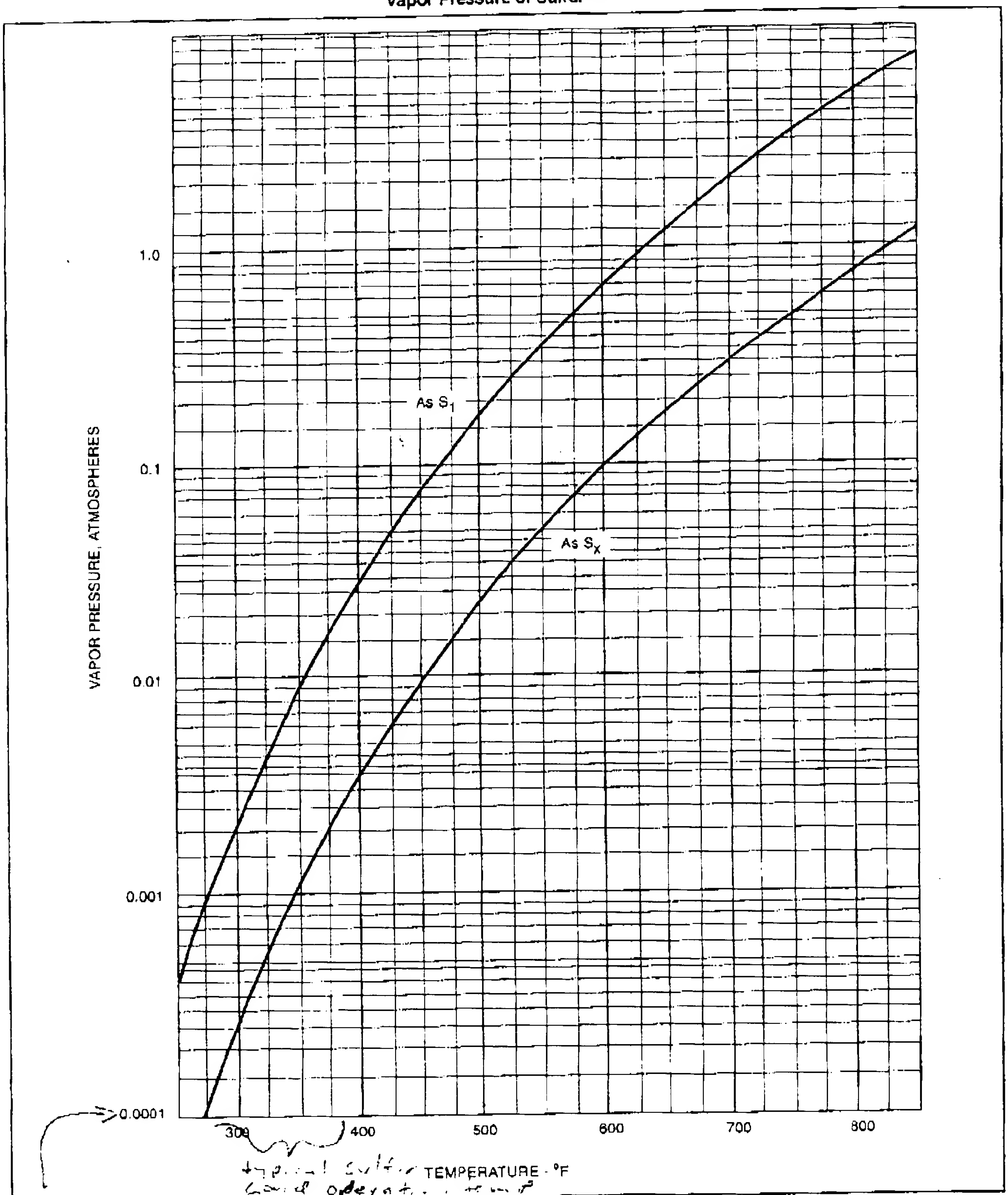
Claus Process: a process in which ⅓ of the H_2S in the acid gas feed is burned to SO_2 which is then reacted with the remaining H_2S to produce sulfur. This is also referred to as the modified Claus process.

Residence Time: the period of time in which a process stream will be contained within a certain volume or piece of equipment, seconds.

Tail Gas Cleanup Unit: a process unit designed to take tail gas from a Claus sulfur recovery plant and remove additional sulfur with the goal of meeting environmental sulfur emission standards.

FIG. 22-20

Vapor Pressure of Sulfur[9, 20]



At DeJong condition .0001 mole frac sulfur, no sulfur would condense at 1 atm total pressure.
At higher total pressure, the mole frac would be even lower,

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